



# $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$ nanocomposites as efficient and stable visible-light-driven photocatalyst for $\text{H}_2$ evolution and $\text{CO}_2$ reduction

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## ABSTRACT

Metal-organic frameworks (MOFs), a new class of porous crystalline materials, have attracted great interest as fascinating materials for sustainable energy and environmental remediation. However, the functionalization and diversification of MOFs are still challenging and imperative for the development of highly active MOF-based materials. In this study, a series of  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  nanocomposites with different UiO-66-NH<sub>2</sub> contents were fabricated via a facile solvothermal method. The photocatalytic performances of the obtained  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  nanocomposites were evaluated by photocatalytic  $\text{H}_2$  evolution and  $\text{CO}_2$  reduction under visible-light irradiation. The resultant hybrids exhibit significantly enhanced photocatalytic activity for hydrogen evolution and  $\text{CO}_2$  reduction as compared with pristine components, and the optimal UiO-66-NH<sub>2</sub> content is 20 wt%. The composite can show a hydrogen evolution rate of 5846.5  $\mu\text{mol h}^{-1} \text{g}^{-1}$  and a  $\text{CH}_3\text{OH}$  production rate of 6.8  $\mu\text{mol h}^{-1} \text{g}^{-1}$ . The remarkable enhancement of the photocatalytic activity should be attributed to the efficient charge separation and transfer on the interface between  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  and UiO-66-NH<sub>2</sub>. Furthermore, the  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  photocatalysts show excellent stability during photocatalytic hydrogen evolution and  $\text{CO}_2$  reduction. This work demonstrates that MOF-based composite materials hold great promise for applications in the field of energy conversion and environmental purification.

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## 1. Introduction

In the past few decades, semiconductor-based photocatalysis has attracted great attention because of its potential for solving energy and environmental problems [1–5]. Among the various photocatalytic reactions, the splitting of  $\text{H}_2\text{O}$  to  $\text{H}_2$  and the reduction of  $\text{CO}_2$  to chemical fuels are two of the most important and challenging reactions. To date, various kinds of photocatalysts, such as  $\text{TiO}_2$  [6],  $\text{BiVO}_4$  [7],  $\text{Bi}_2\text{WO}_6$  [8],  $\text{Zn}_2\text{GeO}_4$  [9],  $\text{Zn}_2\text{Ga}_2\text{O}_4$  [10],  $\text{NaNbO}_3$  [11],  $\text{CdS}$  [12], etc, have been explored for applications in these two reactions. However, the quantum yield and solar energy conversion efficiency of these developed photocatalysts are still relatively low, which limits their practical applications. Therefore, it is still attractive to explore new photocatalysts with low cost, improved activities and high stability.

As the solid solution of  $\text{CdS}$  and  $\text{ZnS}$ ,  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  possesses a tunable composition as well as a band gap. The newly formed energy band in  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  could respond to visible light. Previous studies have revealed that  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  is active for water splitting  $\text{H}_2$ -production and degradation of organic pollutants under visible light irradiation and shows a considerable chemical stability [13–15]. However, the photocatalytic activity of pristine  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  is low because of the poor separation efficiency and low migration ability of the photoexcited charge carriers [1]. Some efforts have been performed to enhance the photocatalytic performance of  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ . For example, by controlling morphologies of  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  [16], doping with noble metals [17], and incorporation of reduced graphene oxide [1,18] or other semiconductors [19], the photocatalytic performance of  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  has been enhanced to a certain degree. Unfortunately, the photocatalytic activity of the  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  photocatalyst is still far from the fundamental requirement of practical application. Thus development of novel approaches for the modification of the  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  photocatalyst is highly desired. Additionally, to the best of our knowledge, there is no report about the  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ -based material used as photocatalyst for  $\text{CO}_2$  reduction so far.

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Metal-organic frameworks (MOFs) are a fascinating class of porous crystalline materials built from metal ions and polyfunctional organic ligands. They have attracted significant research interest in recent years mainly due to their tunable pore sizes, high specific surface areas, the possibility to functionalize, and designable framework structures [20–22]. Taking advantage of these features, MOFs have been widely studied for many applications such as gas storage [23], gas separation [24], heterogeneous catalysis [21,25], nonlinear optics [26], biomedical imaging [27], chemical sensing [28] and drug delivery [22,29]. In addition, recent researches demonstrate some MOFs exhibit semiconductor behavior and can be used as photocatalyst. In fact, more and more photocatalysts based on MOFs applied in the degradation of organic pollutants (e.g. MOF-5, UTSA-38, MIL-100(Fe), MIL-53(Fe), MIL-88A and ZIF-8), hydrogen evolution (UiO-66), CO<sub>2</sub> reduction (e.g. UiO-67, MOF-253, MIL-53(Fe), NH<sub>2</sub>-MIL-125(Ti) and NH<sub>2</sub>-UiO-66), and organic transformations (e.g. UiO-67, MIL-100(Fe), NH<sub>2</sub>-MIL-125(Ti) and NH<sub>2</sub>-MIL-101(Fe)) have already been reported [30–45]. Compared with traditional semiconductor photocatalysts, the MOF photocatalysts are beneficial because various combinations of metal-oxo clusters and bridging organic linkers allow for fine-tuning and rational design of these photocatalysts at the molecular level. Furthermore, intrinsic porosity of MOFs facilitates the diffusion of substrates and products through the open framework structures [46,47]. Despite the rapidly growing interest in MOFs, the studies on MOF-based photocatalysis are still in the infancy stage and the photocatalytic performances of MOFs have yet to be fully exploited. The previous MOFs-derived photocatalysts are still subject to some drawbacks such as low quantum efficiency and poor stability. To enhance the photocatalytic performance of MOFs, some strategies such as metal [48] or ligand substitution [44] and noble metal deposition [49] have been employed. Besides, the formation of heterostructure by coupling MOFs with light-harvesting semiconductor materials is also a feasible route to promote the separation of photogenerated charge carriers and thus increase the photocatalytic activity. Recently, semiconductor@MOF heterostructures like ZnO@ZIF-8 [50], Cu<sub>3</sub>(BTC)<sub>2</sub>@TiO<sub>2</sub> [51], BiVO<sub>4</sub>@MIL-101 [52], Bi<sub>2</sub>WO<sub>6</sub>@UiO-66 [53], BiOBr@UiO-66 [54], UiO-66@g-C<sub>3</sub>N<sub>4</sub> [55], CdS@UiO-66-NH<sub>2</sub> [47] and MoS<sub>2</sub>@UiO-66@CdS [46] have been synthesized and show great advantages due to their synergistic effect. Nevertheless, up to now studies concerning MOF-based hybrid photocatalysts are still scarce. In particular, the photocatalytic activities of Cd<sub>x</sub>Zn<sub>1-x</sub>S@MOF nanocomposites, to the best of our knowledge, have not been investigated.

In this work, we report for the first time a new hybrid photocatalyst made by coupling amino-functionalised Zr-based MOF (UiO-66-NH<sub>2</sub>) and Cd<sub>x</sub>Zn<sub>1-x</sub>S. UiO-66-NH<sub>2</sub> was chosen as the metal-organic framework material owing to its large surface area, excellent thermal and chemical stability, visible-light responsiveness and semiconductor property [46,47,53–56]. Our preliminary experiments showed that, among pristine Cd<sub>x</sub>Zn<sub>1-x</sub>S solid solutions with different stoichiometries, the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S solid solution exhibited the highest photocatalytic activity for H<sub>2</sub>-production and CO<sub>2</sub> reduction. Therefore, Cd<sub>0.2</sub>Zn<sub>0.8</sub>S solid solution was used in this study. Here, we developed a facile solvothermal method to prepare a series of UiO-66-NH<sub>2</sub> supported Cd<sub>0.2</sub>Zn<sub>0.8</sub>S nanocomposites with different UiO-66-NH<sub>2</sub> contents. The obtained Zn<sub>0.8</sub>Cd<sub>0.2</sub>S@UiO-66-NH<sub>2</sub> nanocomposites showed excellent high photocatalytic activity and stability in H<sub>2</sub>-production and CO<sub>2</sub> reduction under visible light ( $\lambda > 420$  nm) irradiation. Furthermore, the possible mechanism for the excellent photocatalytic performance of Zn<sub>0.8</sub>Cd<sub>0.2</sub>S@UiO-66-NH<sub>2</sub> is also proposed. We hope that the current work could inspire growing interest on the fabrication of other high-performance semiconductor@MOFs composite by taking the advantage of MOFs.

## 2. Experimental

### 2.1. Materials

Zirconium tetrachloride (ZrCl<sub>4</sub>), *N,N*-dimethyl formamide (DMF), cadmium acetate dihydrate (Cd(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), zinc acetate dihydrate (Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O), sodium sulfide nonahydrate (Na<sub>2</sub>S·9H<sub>2</sub>O), methanol and ethylene glycol (EG) were purchased from Sinopharm Chemical Reagent Co., Ltd. 2-Aminoterephthalic acid (ATA) was obtained from Tokyo Chemical Industry Co., Ltd. All the reagents were of analytical grade and were used without further purification.

### 2.2. Synthesis

#### 2.2.1. Synthesis of UiO-66-NH<sub>2</sub>

UiO-66-NH<sub>2</sub> was synthesized using the same procedure reported previously [47]. In a typical synthesis, 0.2332 g ZrCl<sub>4</sub> and 0.1812 g ATA were dissolved in 50 mL DMF, and then the mixture solution was transferred to a 100 mL Telton-lined stainless steel autoclave. The autoclave was sealed and heated in an electrical oven at 120 °C for 48 h under autogenous pressure. After cooling naturally, the obtained sample was centrifuged and washed with anhydrous methanol for several times to remove the residual DMF. The final product was dried under vacuum at 100 °C for 12 h.

#### 2.2.2. Synthesis of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub>

The Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites were obtained by a one-step solvothermal method. In detail, 0.133 g Cd(AC)<sub>2</sub>·2H<sub>2</sub>O and 0.439 g Zn(AC)<sub>2</sub>·2H<sub>2</sub>O were dissolved in 30 mL EG to form a homogeneous solution. Meanwhile, an appropriate amount of as-prepared UiO-66-NH<sub>2</sub> sample was dispersed in 10 mL EG by sonication for 0.5 h. The obtained UiO-66-NH<sub>2</sub> solution was added to the above mixed salt solution gradually and stirred for 1 h at room temperature. After that, 10 mL 0.3 M Na<sub>2</sub>S aqueous solution was added dropwise with continuous stirring. After being stirred for 2 h, the suspension was transferred to a 100 mL Teflon-lined autoclave and maintained at 160 °C for 4 h. The final product was collected by centrifugation, washing with ethanol and deionized water, and drying in an oven at 80 °C for 24 h. The as-synthesized Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> samples with 10 wt%, 20 wt%, 30 wt% and 40 wt% UiO-66-NH<sub>2</sub> were labeled as CZS@UN10, CZS@UN20, CZS@UN30 and CZS@UN40 respectively. For comparison, the pure Cd<sub>0.2</sub>Zn<sub>0.8</sub>S sample was also prepared using the same solvothermal method in the absence of UiO-66-NH<sub>2</sub>.

### 2.3. Characterization

The crystal structure of the as-prepared samples was identified by an X-ray diffractometer (XRD, D/MAX-2550) using Cu K $\alpha$  radiation. The morphologies and microstructures of the samples were analyzed by the transmission electron microscope (TEM, JEOL 200CX) with an energy-dispersive X-ray (EDX) spectrometer and high-resolution transmission electron microscope (HRTEM, JEM-2010F). The X-ray photoelectron spectroscopy (XPS) measurement was carried out in PHI ESCA-5000C electron spectrometer. N<sub>2</sub> adsorption-desorption isotherms were obtained at -196 °C on a Micromeritics ASAP 2460 Sorptometer using static adsorption procedures, and the Brunauer-Emmett-Teller (BET) surface areas and pore size distributions were calculated by using N<sub>2</sub> adsorption-desorption isotherms. UV-vis absorption spectra of the samples were recorded on a UV-vis spectrophotometer (Hitachi U-3010) with a wavelength range of 200–800 nm. Photoluminescence (PL) spectra were measured using a Hitachi F-7000 fluorescence spectrophotometer at room temperature. Thermo-gravimetric analysis (TGA) was performed on a TA Q50 thermal analyzer under nitrogen

atmosphere with a heating rate of  $10^{\circ}\text{C min}^{-1}$ . The concentration of the Cd and Zn ions in solution was quantified by an inductively coupled plasma emission spectroscopy (ICP, PERKINE 7300DV).

#### 2.4. Photocatalytic test

The photocatalytic hydrogen evolution experiments were performed at room temperature in a 100 mL quartz reactor, which is connected with a closed-cycle circulation system. The visible light was provided by a 300 W Xenon lamp (PLS-SXE300C, Beijing Perfectlight Co. Ltd., China) coupled with a UV cut-off filter ( $\lambda > 420$  nm). In a typical experiment, 0.05 g of photocatalyst powder was dispersed in 100 mL of aqueous solution containing 0.1 M  $\text{Na}_2\text{S}$  and 0.1 M  $\text{Na}_2\text{SO}_3$ . The reaction vessel was evacuated by  $\text{N}_2$  for 30 min to remove dissolved oxygen before photocatalytic experiments. The reaction cell was kept at room temperature with cooling water. The produced  $\text{H}_2$  was detected using an online gas chromatography (GC7900,  $\text{N}_2$  carrier, 5A molecular sieve column, TCD detector).

The photocatalytic reduction of  $\text{CO}_2$  experiment was conducted in a closed gas circulation system equipped with a 300 W Xe lamp combined with a 420 nm cut-off filter as a light source. All experiments were performed at room temperature. In each run, 0.1 g photocatalyst was dispersed in 100 mL aqueous solution containing 0.1 M NaOH. To prevent the reactor being interfered with outside light, the system was covered by tinfoil. Before irradiation,  $\text{CO}_2$  (99.995%) was bubbled through the reactor for 30 min to eliminate dissolved oxygen and saturate the solution. Then, the suspension was exposed to visible light irradiation under magnetic stirring. At given time intervals, about 1 mL suspensions were collected and centrifuged to remove the photocatalyst particles. The concentrations of reduction product were analyzed using a GC7900 gas chromatography equipped with a FID detector and a capillary column (TM-PLOT U, 30 m  $\times$  0.53 mm  $\times$  20  $\mu\text{m}$ ).

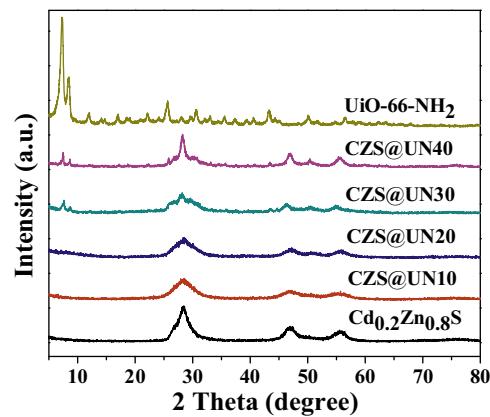
#### 2.5. Photocurrent measurements

Photocurrent measurements were performed on a CHI-660 electrochemical workstation (Chenhua Instrument, Shanghai, China) in a conventional three electrode configuration with a Pt foil as the counter electrode and an Ag/AgCl (saturated KCl) as the reference electrode. A 300 W Xe arc lamp served as a light source. A 0.5 M  $\text{Na}_2\text{SO}_4$  aqueous solution was used as the electrolyte. The working electrodes were prepared as follows: 10 mg of the prepared photocatalyst was ground with 20  $\mu\text{L}$  of a poly (3, 4-ethylenedioxythiophene)/poly(styrenesulfonate) (PEDOT/TPSS, 1.3–1.7%) aqueous solution and 100  $\mu\text{L}$  of distilled water to make a slurry. The slurry was then spread on a 1.5 cm  $\times$  1.0 cm indium-tin oxide (ITO) glass substrate with an active area of about 0.3  $\text{cm}^2$  by the doctor-blade method, using adhesive tape as the space. Finally, the electrode was dried in an oven and annealed at 150  $^{\circ}\text{C}$  for 30 min.

### 3. Results and discussion

#### 3.1. $\text{Cd}_x\text{Zn}_{1-x}\text{S}$ solid solutions

Fig. S1 shows the XRD patterns of  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  samples synthesized by a solvothermal method. The XRD patterns for  $x = 0.0$  and 1.0 are identical to those reported for ZnS [JCPDS No. 05-0566] and CdS [JCPDS No. 10-0454], respectively. With increasing  $x$ , the diffraction peaks shift to smaller-angle side. The gradual shift of the XRD pattern as a function of  $x$  indicates that the samples are not mixtures of ZnS and CdS phases but  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  solid solutions.



**Fig. 1.** XRD patterns of pure  $\text{UiO-66-NH}_2$ ,  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  and  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  composites.

It is well-known that the photocatalytic activity of  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  can be altered by varying the Cd/Zn ratio. Fig. S2 shows that the prepared  $\text{Cd}_x\text{Zn}_{1-x}\text{S}$  solid solution without  $\text{UiO-66-NH}_2$  exhibits the highest photocatalytic activity for  $\text{H}_2$ -production and  $\text{CO}_2$  reduction at  $x = 0.2$ , thus  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  solid solution was used in the following study.

#### 3.2. $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$ composites

##### 3.2.1. Materials characterization

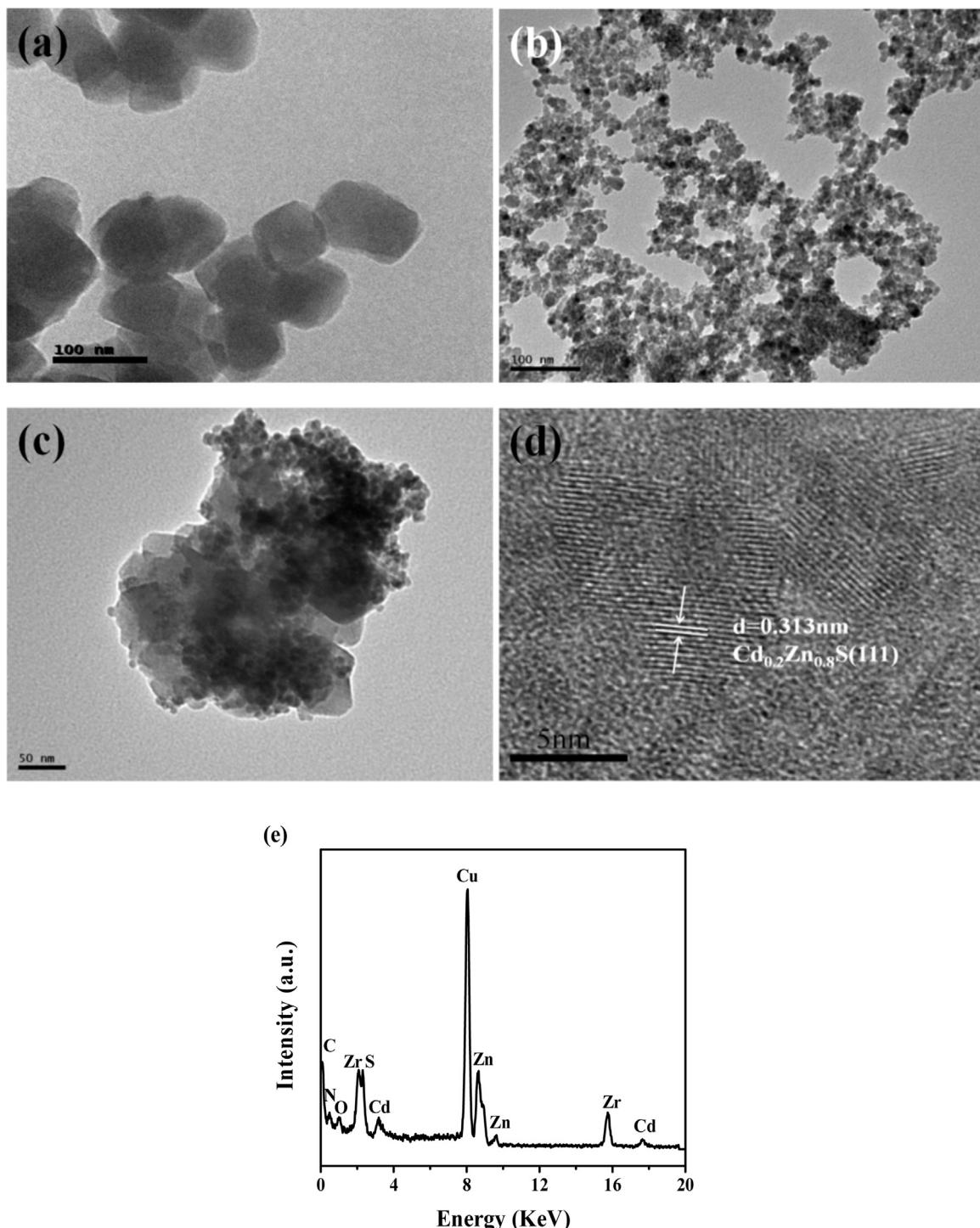
Thermo-gravimetric analysis was performed from room temperature to 800  $^{\circ}\text{C}$  under nitrogen conditions to determine the real content of  $\text{UiO-66-NH}_2$  in the  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  nanocomposites and the results are shown in Fig. S3. From which the residual quantity can be obtained for  $\text{UiO-66-NH}_2$ ,  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  and  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  composites. Then the  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  to  $\text{UiO-66-NH}_2$  mass ratio ( $\frac{m_{\text{CZS}}}{m_{\text{UN}}}$ ) in composites can be calculated by the following equation [52]:

$$\frac{m_{\text{CZS}}}{m_{\text{UN}}} = \frac{r_{\text{CZSUN}} - r_{\text{UN}}}{r_{\text{CZS}} - r_{\text{CZSUN}}},$$

where  $r_{\text{CZSCN}}$ ,  $r_{\text{CZS}}$  and  $r_{\text{UN}}$  are the residual mass fraction (%) of  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$ ,  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  and  $\text{UiO-66-NH}_2$ , respectively. As shown in Table S1, the real  $\text{UiO-66-NH}_2$  contents are nearly consistent with the theoretical values.

Fig. 1 shows the XRD patterns of pure  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$ ,  $\text{UiO-66-NH}_2$ , and  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  nanocomposites with different weight contents of  $\text{UiO-66-NH}_2$ . The XRD pattern of as-synthesized  $\text{UiO-66-NH}_2$  corresponds well to those reported previously [47,57], demonstrating the successful synthesis of  $\text{UiO-66-NH}_2$ . The XRD peaks of pure  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  exhibit an obvious left-shift compared to the standard of sphalerite ZnS due to the formation of  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  solid solution [1,58]. The XRD patterns of  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S@UiO-66-NH}_2$  composites show no obvious diffraction peak attributable to  $\text{UiO-66-NH}_2$  when the  $\text{UiO-66-NH}_2$  content is less than 20 wt%, which may be due to the low content of  $\text{UiO-66-NH}_2$ . However, the composites with higher  $\text{UiO-66-NH}_2$  loading clearly display the diffraction peaks of  $\text{UiO-66-NH}_2$  and  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$ , reflecting a two-phase composition of  $\text{UiO-66-NH}_2$  and  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  in these composites.

The morphologies and microstructures of the as-prepared samples were characterized by TEM and HRTEM. As shown in Fig. 2a, the pure  $\text{UiO-66-NH}_2$  displays a cube morphology, and the size of these cubes is about 50–80 nm. The pristine  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  sample exhibits uniform particle morphology with the diameter of 10–20 nm (Fig. 2b). The TEM image of CZS@UN20 shows that the  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}$  nanoparticles are well dispersed on the surface of the



**Fig. 2.** TEM images of (a) UiO-66-NH<sub>2</sub>, (b) Cd<sub>0.2</sub>Zn<sub>0.8</sub>S, (c) CZS@UN20, (d) HRTEM image of CZS@UN20, and (e) EDX spectrum of CZS@UN20.

UiO-66-NH<sub>2</sub> cubes (Fig. 2c). The high resolution TEM (HRTEM) image (Fig. 2d) of CZS@UN20 shows clear fringes with lattice spacing of ca. 0.313 nm, which corresponds to the (111) plane of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S [1,58]. The EDX spectrum (Fig. 2e) confirms the presence of Cd, Zn, S, Zr, C, O and N elements in the composite.

The composition and chemical state of the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composite were investigated by XPS. The survey spectrum (Fig. 3a) indicates that the sample is composed of C, N, O, Zr, Cd, Zn and S, which is in good agreement with the EDX results. Fig. 3b shows the binding energies of Cd 3d<sub>5/2</sub> and Cd 3d<sub>3/2</sub> peaks at

404.7 and 411.5 eV respectively, which are typical values for Cd<sup>2+</sup> in CdS [15,58,59]. As shown in Fig. 3c, two peaks recorded in the Zn 2p region at 1022.1 and 1045.5 eV are in agreement with the literature data for Zn<sup>2+</sup> in ZnS [15,58,59]. The S 2p core-level spectrum (Fig. 3d) shows two peaks at 161.3 eV and 162.4 eV, which imply that S is in sulfide state [15,58,59]. The curves of Zr 3d region (Fig. 3e) can be deconvoluted into two peaks for Zr 3d<sub>5/2</sub> and Zr 3d<sub>3/2</sub> located at around 182.1 eV and 184.3 eV respectively, which indicates the existence of Zr<sup>4+</sup> [15,58,59]. The C 1s spectrum shown in Fig. 3f can be deconvoluted into three peaks located at

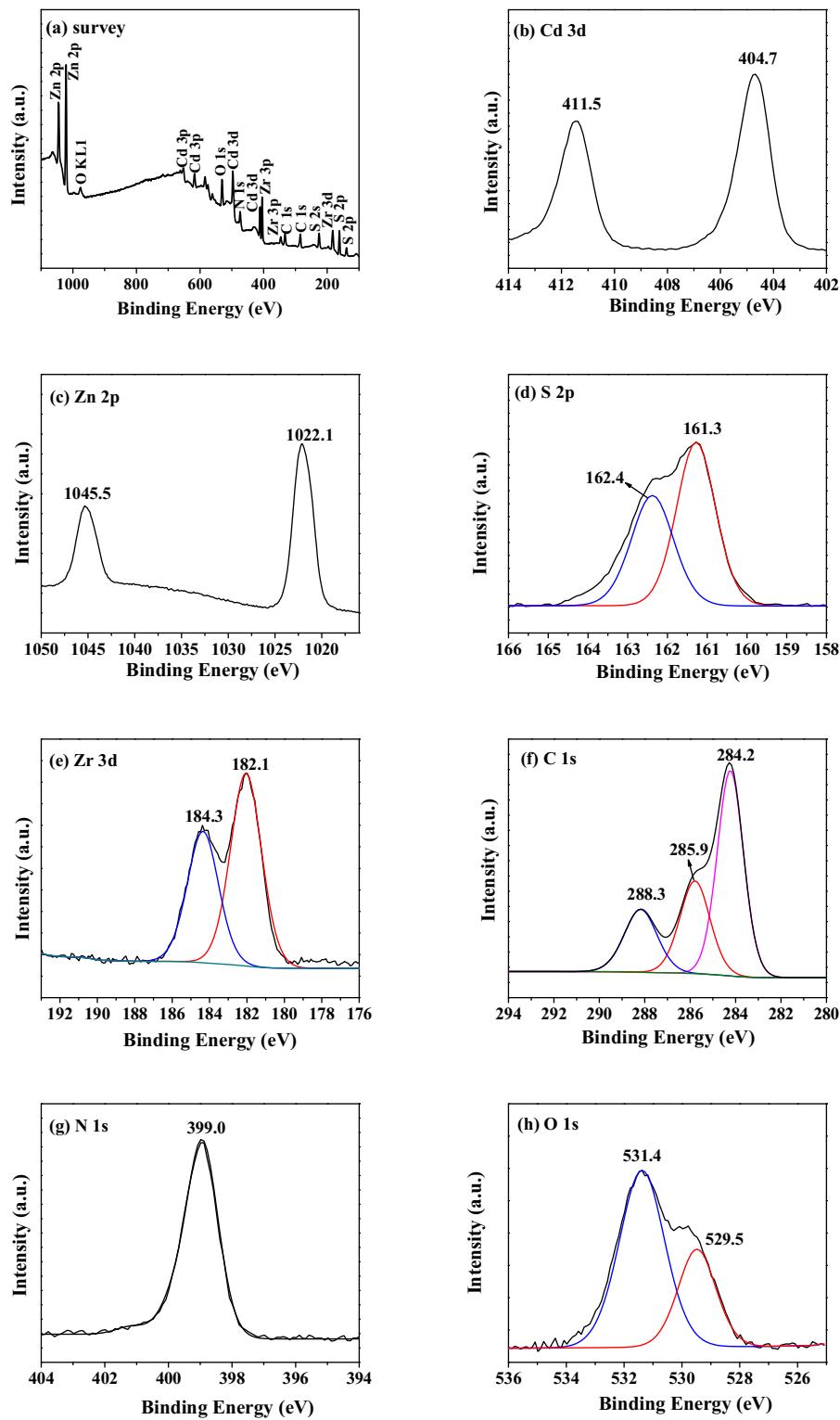
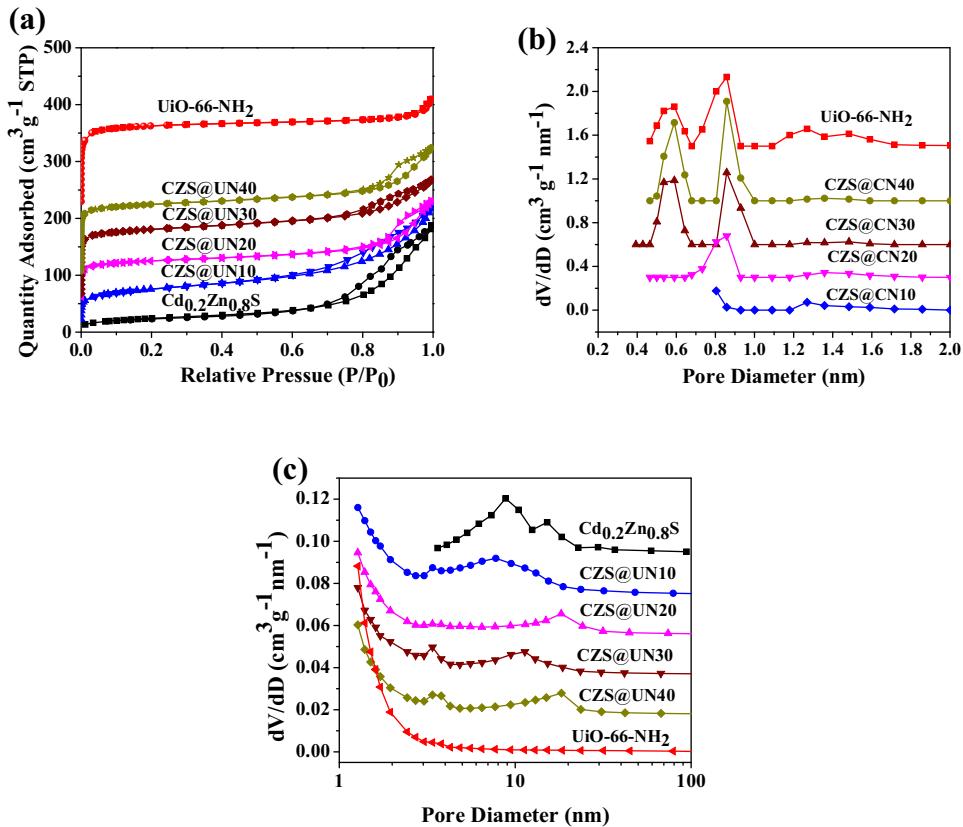


Fig. 3. XPS spectra of CZS@UN20: (a) survey, (b) Cd 3d, (c) Zn 2p, (d) S 2p, (e) Zr 3d, (f) C 1s, (g) N 1s, (h) O 1s.

284.2, 285.9 and 288.3 eV. These three peaks can be assigned to the carbon components on the benzene ring, the C–NH<sub>2</sub> species and the carboxylate (O—C=O) groups of the ATA linkers, respectively [55,60,61]. The N 1s XPS spectrum (Fig. 3g) of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> is located at 399.0 eV, which can be attributed to N species in the NH<sub>2</sub> group [55,60,61]. The high-resolution XPS spectrum of the O 1s orbital can be fitted by two peaks at binding energies of around 531.4 and 529.5 eV (Fig. 3h), which are attributed to the

oxygen components on the carboxylate groups of the ATA linkers and the Zr—O bonds of UiO-66-NH<sub>2</sub>, respectively [55,60,61].

The N<sub>2</sub> adsorption-desorption measurement was carried out to study the specific surface area and porosity of the as-prepared samples, as shown in Fig. 4 and Table 1. The isotherm of UiO-66-NH<sub>2</sub> belongs to the typical type I, indicating its typical microporous structure [62,63]. The Horvath-Kawazoe (HK) micropore size distribution of UiO-66-NH<sub>2</sub> (Fig. 4b) reveals three major pores at 0.6,



**Fig. 4.** (a) N<sub>2</sub> adsorption-desorption isotherms, (b) Horvath-Kawazoe (HK) micropore size distributions, and (c) Barrett-Joyner-Halenda (BJH) mesopore size distributions of as-prepared samples.

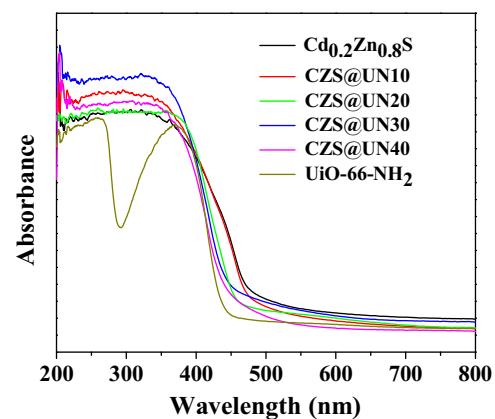
**Table 1**

Summary of textural properties and photocatalytic activities of the samples.

Sample	S <sub>BET</sub> (m <sup>2</sup> g <sup>-1</sup> )	Pore volume (cm <sup>3</sup> g <sup>-1</sup> )	Average Pore Size (nm)	H <sub>2</sub> evolution rate (μmol h <sup>-1</sup> g <sup>-1</sup> )	CH <sub>3</sub> OH production rate (μmol h <sup>-1</sup> g <sup>-1</sup> )
Cd <sub>0.2</sub> Zn <sub>0.8</sub> S	85.2	0.0559	12.02	2804.2	2.0
CZS@UN10	201.0	0.2551	4.75	4591.6	4.1
CZS@UN20	266.0	0.2741	3.26	5846.5	6.8
CZS@UN30	381.3	0.3882	2.46	5235.9	5.9
CZS@UN40	491.1	0.3982	2.43	4922.7	5.3
UiO-66-NH <sub>2</sub>	967.6	0.5626	1.78	0	0

0.9 and 1.3 nm, which agree quite well with the crystal model and previously-reported values [62,63]. The as-prepared Cd<sub>0.2</sub>Zn<sub>0.8</sub>S displays a type IV isotherm with a H3 typical hysteresis loop, indicating the presence of mesoporous structure [64,65]. These mesopores may come from the interstitial voids among Cd<sub>0.2</sub>Zn<sub>0.8</sub>S nanoparticles. All Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> samples exhibit hybrid type I/IV isotherms with large hysteresis between adsorption and desorption branches, revealing the presence of a combination of micropores and mesopores. The existence of both micro- and mesopores can be confirmed by the corresponding pore size distributions as shown in Fig. 4b and c. As shown in Table 1, the BET specific surface areas of pristine UiO-66-NH<sub>2</sub> and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S are 967.6 and 85.2 m<sup>2</sup> g<sup>-1</sup>, respectively. All Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites have higher specific surface areas than Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and the specific surface area of the composites increase with the enhancement of UiO-66-NH<sub>2</sub> contents. Similarly, because of the larger total pore volume of pristine UiO-66-NH<sub>2</sub> than that of pristine Cd<sub>0.2</sub>Zn<sub>0.8</sub>S, the total pore volumes of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites are also increased with the increase of UiO-66-NH<sub>2</sub> content.

The optical absorption of different Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites, pristine UiO-66-NH<sub>2</sub> and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S samples were measured by UV-vis. As illustrated in Fig. 5, the pristine UiO-



**Fig. 5.** UV-vis spectra of pure UiO-66-NH<sub>2</sub>, Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites.

66-NH<sub>2</sub> shows the strong absorption bands in the range of 200–450 nm. The absorption edge value for Cd<sub>0.2</sub>Zn<sub>0.8</sub>S is observed at 500 nm. The Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites have absorp-

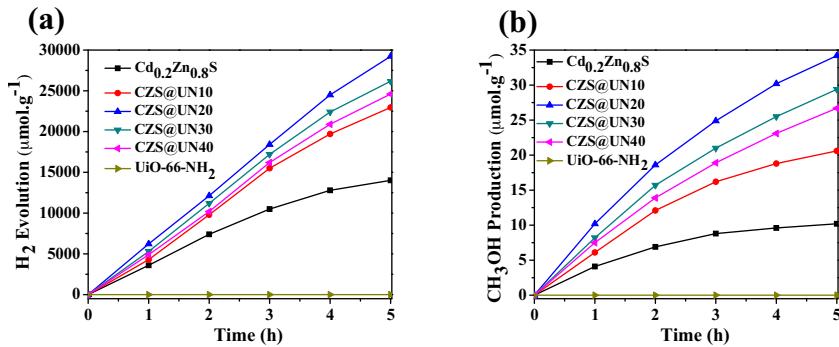


Fig. 6. Plots of (a) photocatalytic H<sub>2</sub> evolution amount and (b) photocatalytic CO<sub>2</sub> reduction amount vs. irradiation time.

tion edges of longer wavelengths in comparison with the pristine UiO-66-NH<sub>2</sub>. Similar phenomena were also observed for other MOF-based photocatalysts [53,54]. The slightly red shift might suggest that the composites can absorb more visible light, which may result in generation of more electron-hole pairs. The band gap of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and HOMO-LUMO gap of UiO-66-NH<sub>2</sub> can be calculated by the following equation:  $\alpha h\nu = A(h\nu - E_g)^{n/2}$ , in which  $\alpha$ ,  $h\nu$ ,  $E_g$ , and  $A$  are the absorption coefficient, Planck constant, the light frequency, the band gap (HOMO-LUMO gap), and a constant, respectively. The value of  $n$  depends on the type of optical transition of the semiconductor ( $n=1$  for direct transition and  $n=4$  for indirect transition). For UiO-66-NH<sub>2</sub> and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S, the  $n$  value of 1 is used [54,58,66]. Therefore, as can be seen from Fig. S4, the corresponding band gap value of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and HOMO-LUMO gap value of UiO-66-NH<sub>2</sub> are estimated to be 2.62 and 2.87 eV, respectively. The band gap energies of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S can be calculated by the following equation:

$$E_{VB} = X - E^e + 0.5E_g,$$

where E<sub>VB</sub> represents valence band (VB) edge potential,  $X$  is the electronegativity of the semiconductor estimated by the geometric mean of the electronegativity of the constituent atoms.  $E^e$  is the energy of free electrons on the hydrogen scale ( $\sim 4.5$  eV),  $E_g$  is the band gap energy of the semiconductor. The conduction band (CB) edge potential ( $E_{CB}$ ) can be determined by  $E_{CB} = E_{VB} - E_g$ . The  $X$  value of pure Cd<sub>0.2</sub>Zn<sub>0.8</sub>S is about 5.25 eV. The  $E_{VB}$  of bare Cd<sub>0.2</sub>Zn<sub>0.8</sub>S can be assigned to be +2.06 eV, and the corresponding  $E_{CB}$  of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S can be estimated to be -0.56 eV. Some researches reveal that LUMO potential of UiO-66-NH<sub>2</sub> is at -0.60 eV [47,57], thus its HOMO potential is at 2.27 eV.

### 3.2.2. Photocatalytic activity

The photocatalytic H<sub>2</sub>-production over the as-prepared Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites was evaluated under visible light irradiation ( $\lambda > 420$  nm) using Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub> as sacrificial agents. As shown in Fig. 6a and Table 1, the photocatalytic H<sub>2</sub>-production rate is negligible when UiO-66-NH<sub>2</sub> alone is used as photocatalyst, indicating that UiO-66-NH<sub>2</sub> did not act as an effective photocatalyst by itself. Pristine Cd<sub>0.2</sub>Zn<sub>0.8</sub>S shows some photocatalytic H<sub>2</sub>-production activity, but the rate of H<sub>2</sub> evolution is low ( $2804.2 \mu\text{mol h}^{-1} \text{g}^{-1}$ ). After the introduction of UiO-66-NH<sub>2</sub>, the H<sub>2</sub>-production performance of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S is significantly enhanced. The photoactivity of the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites is found to be dependent on the content of UiO-66-NH<sub>2</sub>. With the increased content of UiO-66-NH<sub>2</sub> from 10 wt% to 20 wt%, the photocatalytic H<sub>2</sub> evolution rate of the hybrid catalyst increases from 4591.6 to 5846.5  $\mu\text{mol h}^{-1} \text{g}^{-1}$ . A further increase in the content of UiO-66-NH<sub>2</sub> leads to a reduction in the photocatalytic activity. This decrease is probably due to the following

factors: (i) accompanying with the increase of UiO-66-NH<sub>2</sub>, the content of the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S, which is the only activity phase, will be decreased relatively. (ii) overmuch UiO-66-NH<sub>2</sub> may turn into a recombination center of photoinduced charges (this can be confirmed by the photoluminescence measurement as shown in Fig. 8a), which will cause reduction of activity. The maximum photocatalytic H<sub>2</sub> generation rate ( $5846.5 \mu\text{mol h}^{-1} \text{g}^{-1}$ ) is obtained when the UiO-66-NH<sub>2</sub> content is 20 wt%, which is about 2.1 times higher than that of pure Cd<sub>0.2</sub>Zn<sub>0.8</sub>S.

The photocatalytic activities of the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites were also evaluated by using them for the photoreduction of CO<sub>2</sub> dissolved in NaOH solutions under visible-light irradiation. Control experiments indicate that no appreciable reduction products were detected in the absence of either photocatalyst or light irradiation, indicating that all the products obtained during the reaction were produced by the photocatalysts. The photocatalytic activity results for all the samples toward the conversion of CO<sub>2</sub> with H<sub>2</sub>O are shown in Fig. 6b and Table 1. Only methanol is detected as a product using Cd<sub>0.2</sub>Zn<sub>0.8</sub>S or the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites as photocatalysts, which is in line with the previous published work that CH<sub>3</sub>OH is the main reduction product in aqueous CO<sub>2</sub> photoreduction systems [67–69]. It can be observed that pristine UiO-66-NH<sub>2</sub> is not active for photocatalytic CO<sub>2</sub> reduction. The bare Cd<sub>0.2</sub>Zn<sub>0.8</sub>S without UiO-66-NH<sub>2</sub> shows a low photocatalytic activity for CO<sub>2</sub> reduction, in which the CH<sub>3</sub>OH production rate is only  $2.0 \mu\text{mol h}^{-1} \text{g}^{-1}$ . All the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> samples exhibit a superior photocatalytic activity for reduction of CO<sub>2</sub> compared with the bare Cd<sub>0.2</sub>Zn<sub>0.8</sub>S. The UiO-66-NH<sub>2</sub> content has a significant influence on the photocatalytic activity of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S. Among the as-prepared samples, CZS@UN20 presents the highest CH<sub>3</sub>OH evolution amount ( $6.8 \mu\text{mol h}^{-1} \text{g}^{-1}$ ) during visible-light irradiation, which is about 3.4 times higher than that of pure Cd<sub>0.2</sub>Zn<sub>0.8</sub>S.

The catalyst lifetime is of great importance besides the photocatalytic performance. The CZS@UN20 hybrid was used as the representative sample to examine the long-term stability of the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites for photocatalytic H<sub>2</sub> production and CO<sub>2</sub> reduction. As shown in Fig. 7a and b, after four recycles, both the H<sub>2</sub> evolution rate and the activity of photocatalytic CO<sub>2</sub> reduction did not show a significant decrease. The structure of the CZS@UN20 sample before and after four consecutive cycles was also recorded by XRD. As shown in Fig. S5, no apparent change in the crystalline structure is observed before and after the reaction. Moreover, the ICP results (Table S2) demonstrate that the leaching of the cadmium and zinc ions is so small that it can be ignored. Based on the above results, it clearly suggests that the as-prepared Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites have relatively high stabilities during photocatalytic H<sub>2</sub> production and reduction of CO<sub>2</sub>.

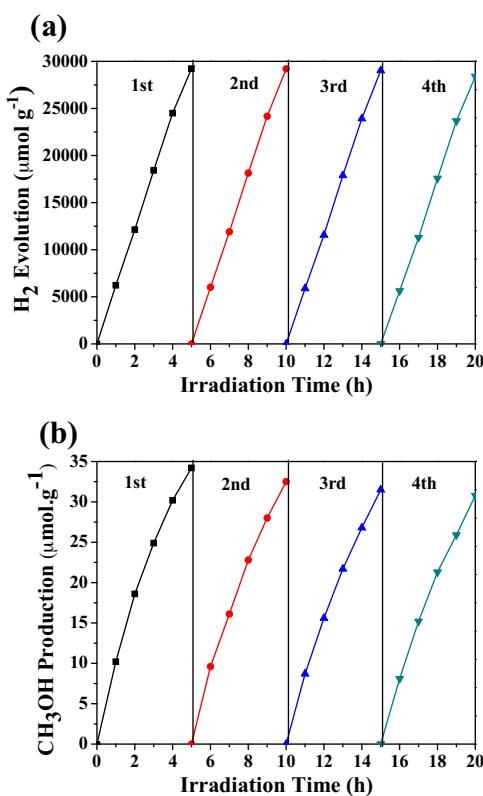


Fig. 7. Cycle runs of (a) photocatalytic H<sub>2</sub> production and (b) CO<sub>2</sub> reduction over the CZS@UN20 photocatalyst.

### 3.2.3. Enhanced visible-light photocatalytic activity mechanism

In order to understand the enhanced photocatalytic mechanism of the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites, PL spectroscopy measurements to analyze the charge recombination of semiconductor were investigated. Fig. 8a presents the PL spectra of pure Cd<sub>0.2</sub>Zn<sub>0.8</sub>S, CZS@UN10, CZS@UN20, CZS@UN30 and CZS@UN40 samples at room temperature with an excitation wavelength of 360 nm. As observed from Fig. 8a, the pure Cd<sub>0.2</sub>Zn<sub>0.8</sub>S exhibits a strong emission peak at around 475 nm. When the UiO-66-NH<sub>2</sub> was added, the PL emission intensity decreases markedly, which suggests that the photoinduced charge could be efficiently separated when the heterojunction was formed between UiO-66-NH<sub>2</sub> and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S. The order of PL intensity is Cd<sub>0.2</sub>Zn<sub>0.8</sub>S > CZS@UN10 > CZS@UN40 > CZS@UN30 > CZS@UN20, which agrees well with the observed results of their photocatalytic activity mentioned above.

The improved carrier separation efficiency of the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composites was further confirmed by the transient photocurrent responses of UiO-66-NH<sub>2</sub>, Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and CZS@UN20. As shown in Fig. 8b, the pure UiO-66-NH<sub>2</sub> sample shows a very low photocurrent density, which can be attributed to the fast recombination of photogenerated electrons and holes in UiO-66-NH<sub>2</sub>. The pure Cd<sub>0.2</sub>Zn<sub>0.8</sub>S has photocurrent under visible light irradiation, corresponding to the photo excitation of the semiconductor. The Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composite shows the highest photocurrent density, indicating the efficient photo-generated charge transfer between Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and UiO-66-NH<sub>2</sub>. The PL and photocurrent results confirmed the superior charge transfer and recombination inhibition in the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composite photocatalyst, which is responsible for the enhanced photocatalytic activity.

On the basis of the above results, a possible interface electron transfer behavior and the corresponding photocatalytic mechanisms for H<sub>2</sub> production and CO<sub>2</sub> reduction are demonstrated and illustrated in Scheme 1. Under visible-light irradiation, UiO-66-NH<sub>2</sub> and Cd<sub>0.2</sub>Zn<sub>0.8</sub>S were excited to generate electron-hole pairs. Since the LUMO potential of UiO-66-NH<sub>2</sub> (−0.60 eV vs. NHE) is more negative than the CB potential of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S (−0.56 eV vs. NHE), the photoinduced electrons on the LUMO of UiO-66-NH<sub>2</sub> can directly transfer to the CB of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S, which could inhibit the recombination of photoinduced electron-hole pairs and prolong the lifetime of photoinduced charge carriers. In the photocatalytic H<sub>2</sub> production, the electrons at the CB of Cd<sub>0.2</sub>Zn<sub>0.8</sub>S can reduce the adsorbed H<sup>+</sup> to evolve H<sub>2</sub>. The holes at the VB (HOMO) were consumed by the sacrificial reagents (Na<sub>2</sub>S and Na<sub>2</sub>SO<sub>3</sub>). In the case of the photocatalytic CO<sub>2</sub> reduction, the active valence band (HOMO) holes can oxidize H<sub>2</sub>O to produce •OH, which can release O<sub>2</sub> and H<sup>+</sup> [70]. Then, H<sup>+</sup> and the CB electrons would reduce CO<sub>2</sub> to CH<sub>3</sub>OH [70].

## 4. Conclusions

In summary, highly active Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> composite photocatalysts have been successfully synthesized by a facile solvothermal process. The resultant hybrids exhibited significantly enhanced photocatalytic activity for hydrogen evolution and CO<sub>2</sub> reduction under visible light irradiation as compared with pristine components. The optimum loading content of UiO-66-NH<sub>2</sub> is determined to be ~20 wt% and the corresponding H<sub>2</sub> evolution rate and CH<sub>3</sub>OH production rate are 5846.5 μmol h<sup>-1</sup> g<sup>-1</sup> and 6.8 μmol h<sup>-1</sup> g<sup>-1</sup>, respectively. The remarkable enhancement of photocatalytic activity can be ascribed to the efficient charge separation and transfer on the interface between Cd<sub>0.2</sub>Zn<sub>0.8</sub>S and UiO-66-NH<sub>2</sub>. Moreover, the Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> photocatalysts exhibited good recyclability under visible-light irradiation. The Cd<sub>0.2</sub>Zn<sub>0.8</sub>S@UiO-66-NH<sub>2</sub> hybrids introduced in this work, with high photocatalytic activity and excellent photostability, are a very

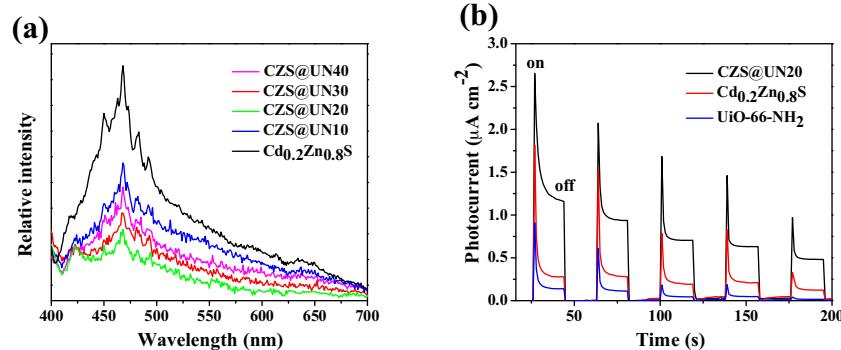
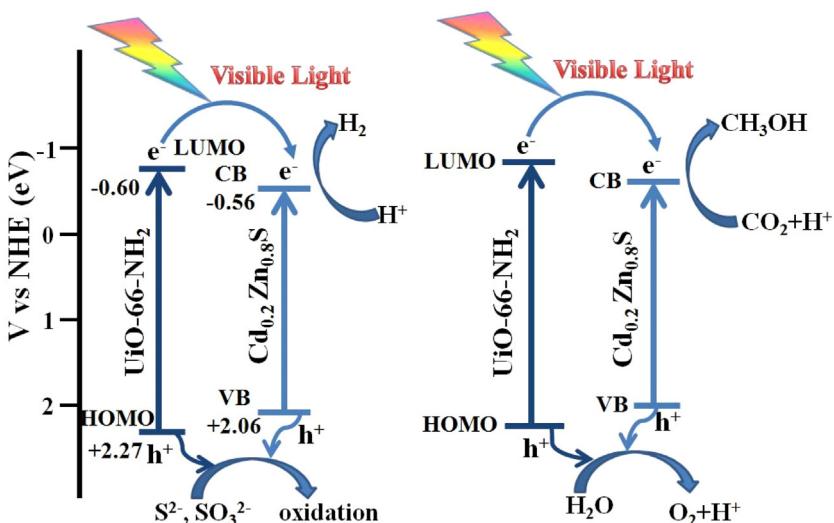


Fig. 8. (a) PL spectra and (b) photocurrent spectra of the as-synthesized samples.



**Scheme 1.** Schematic diagram of the photogenerated electrons and holes transfer in the  $\text{Cd}_{0.2}\text{Zn}_{0.8}\text{S}@\text{UiO-66-NH}_2$  composite and the mechanism of photocatalytic  $\text{H}_2$  production and  $\text{CO}_2$  reduction under visible light irradiation.

promising candidate for possible practical application in high-performance  $\text{H}_2$  production and  $\text{CO}_2$  reduction.

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.apcatb.2016.07.032>.

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